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1. Introduction

The adsorbate H_2O-NaCl(001) dominated by physical interactions is of importance as a strongly polar, H-bonded system in a highly non-uniform electrostatic field. Water not only physically adsorbs on the surface to form an adlayer, but also reacts chemically at defects on the NaCl(001) surface. The cases from the isolated admolecule up to the monolayer collective behavior are of basic interest.

The adsorption of water on salt is significant for numerous phenomena ranging from interstellar dust grains to biochemistry, from sea salt spray, heterogeneous nucleaction of clouds to industrial applications, such as catalysis, nuclear waste deposition in geologically stable rock salt domes. In particular, it is estimated that 10^9 to 10^{11} tons of salt are injected annually as aerosols into the atmosphere from the oceans. The tropospheric reactions of the salt aerosols with NO_2 produce $NaNO_3$ and HCl. The role of adsorbed water in this transformation process is not understood. Another topic of scientific, economic and social relevance especially in northern Germany is the industrial processing of raw mineral salts. In a new electrostatic process, named ESTA, NaCl, KCl, $MgSO_4$ are separated by contact charging after adsorption of water and proper acid vapor from air of defined humidity. Presently some 10^7 tons of mineral salt per year are separated in the ESTA process. More work needs to be done to understand the role of adsorbed water on the salt surface in order to further improve the process.

Systematic studies under well-defined conditions are being carried out on the interaction between water vapor and the clean, monocrystalline NaCl(001) surface under ultrahigh vacuum (UHV) conditions. The surfaces are prepared either by cleaving single crystals in-situ under UHV or under nitrogen gas. Perfect terraces, as far as can be monitored, extending up to 0.5 µm and mono- and poly-atomic steps, color centers and other defects are generated.

This short paper only allows a partial report of the results. A more complete report will be published later.

2. Methods

A variety of experimental and theoretical methods are applied to elucidate the complexities of water adsorption and dissociation on the NaCl surface. In-situ polarization infrared lead

* Short publication of the lecture held in the „Klasse für Naturwissenschaften und Mathematik“.

salt diode laser and Fourier transform spectroscopy of the surfaces, PIRSS, having the advantage of being non-invasive, are used, both in transmission and attenuated total reflection, together with X-ray-photoelectron spectroscopy , atomic force microscopy AFM and low energy electron diffraction LEED at currents below nano-amperes to minimize transformation of the surface by electrons. Highest sensitivity (10^{-4} monolayer CO_2 on NaCl(001)), resolution (better than 10^{-3} cm^{-1}) and polarization are attained in PIRSS.

3. H_2O - NaCl(001)

Structural and dynamic properties of H_2O adsorbed on the NaCl(001) crystal surface were determined in the range of temperatures and partial pressures from 15K to 300K and 2×10^{-10} to 10^3 mbar, respectively. There are main infrared absorptions of the OH-stretching vibrations between 3050 and 3600 cm^{-1}, very broad (100 - 300 cm^{-1}) and red-shifted with respect to the gas frequencies by 200 cm^{-1} and more showing strong hydrogen bonds. The infrared absorptions are polarized, the angle between the NaCl(001) surface and the mean transition dipole moment associated with the symmetric ν_1 and antisymmetric ν_3 H_2O stretching vibration and possibly the first overtone of the bending vibration ν_2 being 20°.

Upon dosing stepwise at 150±2K, $p(H_2O) \leq 8 \times 10^{-8}$ mbar , island growth of the adsorbate from about 1/5 of the saturation coverage Θ_s up to saturation takes place, as indicated by the uniform increase of the integrated absorption A_{int} of the bands at 3500 and 3300 cm^{-1} up to A_{int} =(0.29±0.02) cm^{-1} and A_{int}=(0.20±0.02) cm^{-1} for s-polarization, the angle of IR incidence being 50°. Near saturation an additional band at 3400 cm^{-1} with A_{int}= 0.04 cm^{-1} and shoulders on the low frequency side of all bands emerge. The bands are better resolved in s- than in p-polarization. The corresponding A_{int} values for p-polarization are 0.22, 0.15, 0.06 cm^{-1} for the 3500, 3300 and 3400 cm^{-1} bands. Increase of the partial water pressure $p(H_2O)$ up to 1×10^{-7} mbar does not change the integrated absorption, whereas decrease below 8×10^{-8} mbar causes desorption within an hour. Thus adsorption – desorption equilibrium is established within this period. Dangling OH in H_2O-NaCl(001) normal to the surface is detected in the IR-frequency range around 3700 cm^{-1} only in the more sensitive attenuated total reflection geometry and not in transmission.

At (150±2)K, $p(H_2O) \geq 1 \times 10^{-7}$mbar multilayer condensation sets in with peak absorption at 3225 cm^{-1} and bands at 3370, 3290, 3260 and 3150 cm^{-1}. The spectrum is in agreement with that of polycrystalline ice I_h.

In multilayer condensation at 120K amorphous ice with a broad absorption centered at 3400 cm^{-1}, width 400 cm^{-1}, is formed. An additional weak, sharp band at 3700 cm^{-1} polarized normal to the NaCl(001) surface indicates dangling OH oriented normal to the surface.

Cooling of the saturated adsorbates H_2O-NaCl(001) and D_2O-NaCl(001) at constant coverage, ensured by simultaneous decrease of the H_2O partial pressure, does not produce appreciable changes in the PIRS-spectra.

4. D_2O - NaCl(001). Adsorption Isotherms.

The adsorbate D_2O-NaCl(001) was prepared in order to confirm the interpretation of the observations on the adsorbate H_2O-NaCl(001). At 154.5K the beginning of the D_2O adsorption at 1.5×10^{-8} mbar is observed in both p- and s-polarization at 2600 and 2500 cm^{-1} , the band at 2600 cm^{-1} being more intense and emerging earlier. The bands grow strongly in the range of 4 to 5×10^{-8} mbar up to leveling off; on the low frequency side weaker broad bands evolve being better resolved in s-polarization (2435, 2380, 2340 cm^{-1}). Upon further D_2O- pressure increase from 5×10^{-8} to 1.25×10^{-7} mbar there is almost no change in the spectra, corresponding to saturation. The total integrated absorption is 0.2 cm^{-1} in both p- and s-polarization. At 1.25×10^{-7} mbar new bands at 2480, 2430, 2330 cm^{-1} grow rapidly showing multilayer condensation with the formation of D_2O - 3D ice I.

Further measurements of the adsorption isotherms for D_2O-NaCl(001) in the temperature range between 140 and 157K by means of PIRSS yielded similar results. Steep rises in the isotherms indicate two-dimensional condensation and saturation of the adsorbate before three-dimensional phases grow. The isotherms have plateaus, rising slightly and independent of temperature for both s- and p-polarization and an angle of incidence of 50°, at an integrated absorption of $A_{int} = (0.20 \pm 0.02)$ cm^{-1} in the OD stretching range between 2200 and 2800 cm^{-1}.

In the region of the plateau A_{int} rises by about 20%. At the foot of the steep rise there are bands around 2600 and 2500 cm^{-1} having widths of 50 to 100 cm^{-1} and a total integrated absorption A_{in} of about 0.03 cm^{-1} indicating hydrogen bonds also in the D_2O low coverage range.

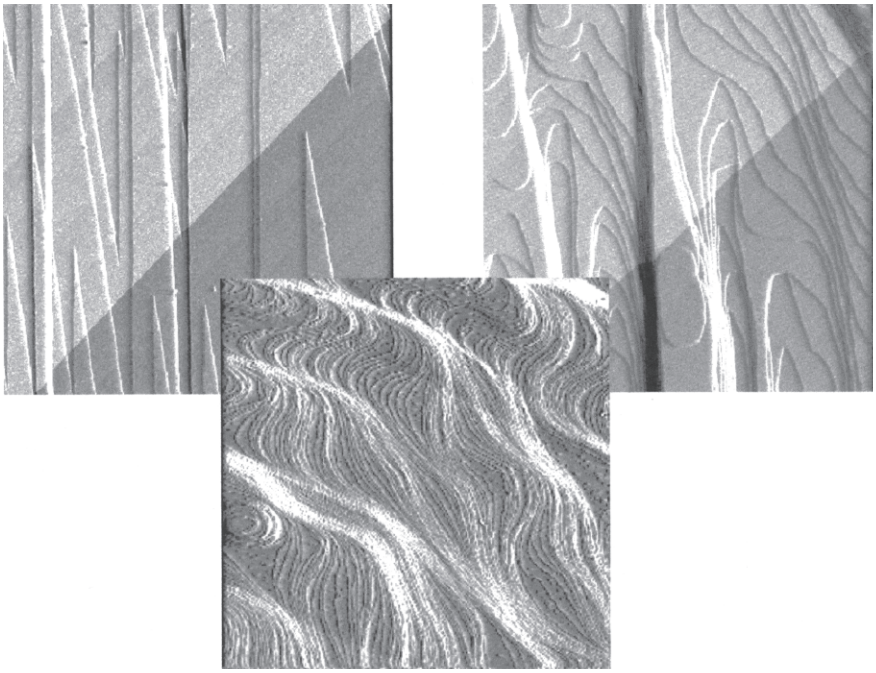
5. Coverage and Lattice Symmetry of H_2O-NaCl(001)

The coverage of the adsorbate H_2O-NaCl(001) and D_2O-NaCl(001) was determined by means of X-ray photoelectron spectroscopy using the O_{1s} photoelectron intensity of the complete monolayer of CO_2 on NaCl(001) as a reference. The coverage is $\Theta = (2.0 \pm 0.3)$ $H_2O(D_2O)$ molecules per Na^+ at the onset of saturation of the 2D-condensed adsorbate layer and rises up to 3 before 3D growth. PIRS-spectra of the 2D-condensed adsorbate D_2O-NaCl(001) at 145K before and after the XPS study do not differ indicating that there are no effects of XPS on D_2O-NaCl(001) detectable by PIRSS.

SPA-LEED studies were performed to determine the lattice symmetry of saturated 2D condensed H_2O (D_2O)-NaCl(001), which was prepared under PIRSS control. In addition, the process of adsorption and two-dimensional condensation was observed by following the specular electron beam intensity scattered from the NaCl(001) surface during the adsorption of water. At constant crystal temperature of 142K the water vapor pressure was increased in small steps. The intensity of the reflected electron beam starts slightly falling at 4×10^{-10} mbar, drops strongly at 1.4 to 1.6×10^{-9} mbar and then falls slightly again up to 7.5×10^{-9} mbar where it drops more strongly again, indicating the regions where the 2D clusters, the 2D condensation, the saturated 2D condensed layer, further adsorption thereon and the 3D growth exist.

Angular distributions of the scattered intensity at various electron energies were measured for the saturated 2D condensed layer of H_2O and D_2O on NaCl(001), the measuring time being ≤0.31 h, the gate time 15 ms. No diffraction peaks were observed in addition to those observed for the base NaCl(001) surface. There is no evidence for any larger superlattice. However, there are significant changes in the ratio of the specular to the diffracted peak intensities, showing a change of the form factor corresponding to a change in the surface corrugation. At 69 eV electron energy, the (0,0) intensity decreases, whereas the (0,1) intensity increases relatively, upon adsorption. The widths of the diffraction peaks appear to remain unchanged. It is concluded that the saturated two-dimensional condensed layer of H_2O forms an ordered (1×1) commensurate layer on the NaCl(001) surface.

If the scan time is increased up to ≥8.5 h, the reflexes of a c(4 × 2) superstructure of the saturated 2D condensed layer of D_2O-NaCl(001) were observed, indicating the conversion



A) Surface prepared by cleaving in-situ under UHV

B) after 30 min. in H_2O vapor at 10mbar, 298K

C) after 2 days in ambient air.

Fig.1 Change of the cleavage structure of the NaCl(001) surface observed by atomic force microscopy. Image section 2μm × 2μm.

of (1×1) H_2O-NaCl(001) into c(4×2) H_2O-NaCl(001) induced by electron impact. The phase c(4×2) H_2O-NaCl(001) had been found by LEED before by M. Henzler et al. on well-ordered atomically thin NaCl films grown heteroepitaxially on Ge(001) substrates.

In a helium atom scattering study a (1 × 1) diffraction pattern was found for the saturated 2D condensed layer by L.W. Bruch, A. Glebov, A.J.P. Toennies and H. Weiss. ELS-LEED studies on H_2O-NaCl(001) film/Ge(001) by M. Henzler and co-workers confirmed the c (4 × 2) structure which is preferentially formed on surfaces with high density of color centers, whereas on surfaces with low density of color centers a c(12 × 2) structure was detected. The spot widths in the diffraction pattern are of the same order as that for the NaCl(001) film/Ge(001) substrate and distinctly smaller than for the c(4 × 2) structure. We conclude that the Gibbs free energies for various adsorbate structures do not differ essentially even at temperatures around 150K. Local perturbations by color centers and steps appear to cause long range effects in the monolayers of water due to strong lateral interactions, especially directed hydrogen-bonding, comparable in strength to the molecule substrate interaction.

6. Water Adsorption Stimulating Ion Mobility on the NaCl(001) Surface. Contact Equilibrium at the Interface of Adsorbate-Covered NaCl and KCl Crystals

The effect of water vapor on the original NaCl(001) surface, prepared by cleaving a single crystal under exclusion of water, is being studied in-situ by ultra high vacuum atomic force microscopy. The first investigation of the cleavage structure of the NaCl(001) surface and the interaction with water was carried out electron-microscopically by H.Bethge, H. Höche et al. using the gold decoration technique.

We observed nanoscale changes of the cleavage structure of the NaCl(001) surface at 298K and very low relative water vapor pressures, $p(H_2O)/p_a \geq 2 \times 10^{-7}$, $p_a = 10$ mbar being the vapor pressure at which the 2D phase transition with the onset of island formation of the adsorbed water layer occurs. Hillocks with base lengths up to 70 nm and heights up to 5 nm are formed at 298 K and $p(H_2O)/p_a = 2 \times 10^{-7}$ within 1 hour, predominantly at defect sites. In time also pits are produced on terraces after 3 hours with diameters in the 50 nm range. Under higher water vapor pressure the structural changes of the in-situ cleaved surfaces of NaCl take place at the typical lightning-shaped step configuration. Above 3 mbar (10% relative humidity) the tips become rounded due to edge-diffusion of salt ions along the monoionic surface steps. Under ambient conditions spontaneous motion of cleavage steps is observed above 30% relative humidity on NaCl(001) surfaces. The step velocity lies in the range of 2 nm/s, depending on the step-shape and the relative humidity. Polyatomic steps convert to several monoatomic steps and an ion transport from upper to lower terraces is observed.

The contact equilibrium at the interface of two adsorbate-covered insulators has been introduced. In particular the contact charging of NaCl versus KCl crystals stimulated by adsorption of water vapor and proper substances such as salicylic acid has been investigated.

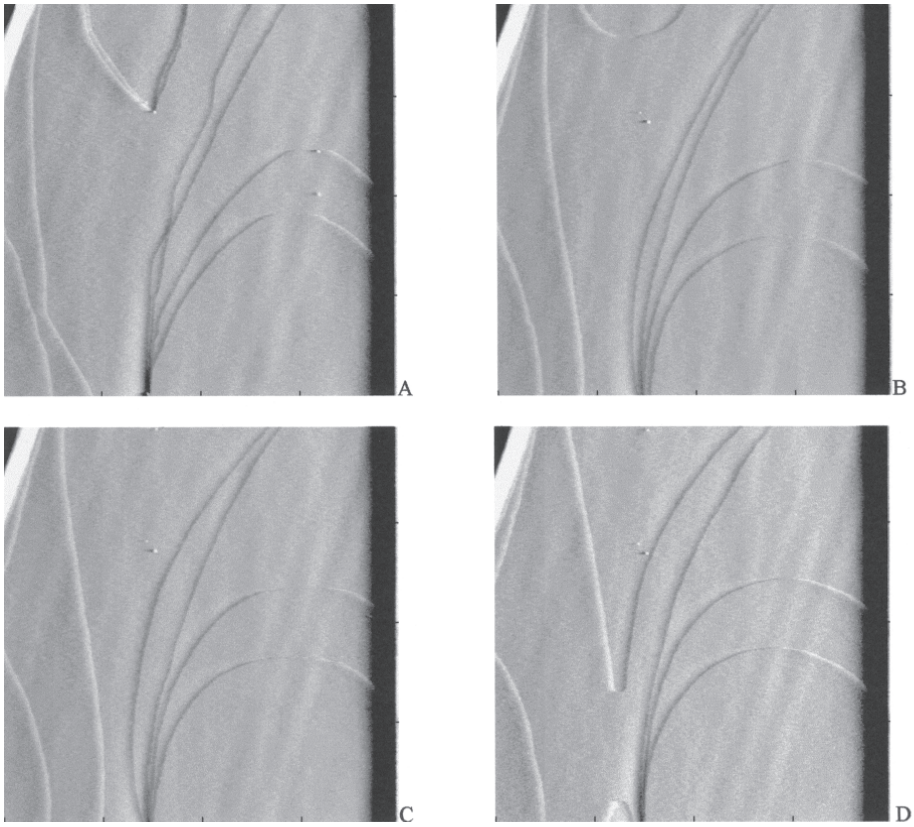


Fig. 2 Migration of monoatomic steps on the NaCl(001) cleavage surface at 53% relative humidity and room temperature (298K) observed by atomic force microscopy. Velocity of step migration 0.5 to 2.0 nm/s. Material transport from upper to lower terrace. Normal force mode(FN). Image section 8µm × 8µm.
A) Start image. Relative humidity <30%.
B) The same surface section after 14min. of 53% relative humidity.
C) 8 min. after B.
D) 8 min. after C.

The pertinent relations of thermodynamics and electrostatics have been applied to the contact equilibrium and charging. Distribution equilibria of mobile ions, electrons and neutrals, chemical equilibria, such as acid-base- and redox-equilibria, have been described. The simplest model of the interface is the HELMHOLTZ-double-layer. The introduction of the new principle of the adsorbate-stimulated contact equilibrium is promoted by the success of the electrostatic separation of mineral salts, the ESTA-process, which was developed on empirical grounds by Kali & Salz GmbH.

7. Acknowledgements

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